

【物件名】

刊行物 2

【添付書類】

刊行物 2

8



134

(19) 日本国特許庁 (JP)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開2001-239156

(P2001-239156A)

(43) 公開日 平成13年9月4日(2001.9.4)

(51) Int. Cl.

識別記号

FI

テマコード (参考)

B01J 20/18

B01J 20/18

D 3L093

C01B 39/02

C01B 39/02

4G066

F25B 17/08

F25B 17/08

Z 4G073

審査請求 未請求 請求項の数 8 OL (全 8 頁)

(21) 出願番号 特願2000-56253(P2000-56253)

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(22) 出願日 平成12年3月1日(2000.3.1)

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(54) 【発明の名称】 ヒートポンプ用吸着剤並びにこれを用いたヒートポンプ

(57) 【要約】

【課題】 合成ゼオライトを用いて極めて効率よく熱交換をするヒートポンプ用吸着剤を提供する。

【解決手段】 本発明は、合成ゼオライト中の交換可能な総電荷の33.3%以上を他の金属イオンで置換した金属置換合成ゼオライトからなるヒートポンプ用吸着剤である。置換する他の金属イオンは2価の金属イオンからなり、例えば Mg^{2+} 、 Ca^{2+} 、 Ba^{2+} 、 Sr^{2+} 、 Mn^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ge^{2+} 、 Sn^{2+} 又は Pb^{2+} から選ばれた少なくとも1種の金属イオンである。あるいは、他の金属イオンが K^{+} 又は Ag^{+} の1価の金属イオンからなるヒートポンプ用吸着剤である。

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【特許請求の範囲】

【請求項1】 合成ゼオライト中の交換可能な総電荷の33.3%以上を他の金属イオンで置換してなる金属置換合成ゼオライトからなることを特徴とするヒートポンプ用吸着剤。

【請求項2】 前記他の金属イオンが2価の金属イオンからなる請求項1記載のヒートポンプ用吸着剤。

【請求項3】 前記2価の金属イオンが Mg^{2+} 、 Ca^{2+} 、 Ba^{2+} 、 Sr^{2+} 、 Mn^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ge^{2+} 、 Sn^{2+} 又は Pb^{2+} から選ばれた少なくとも1種の金属イオンである請求項2記載のヒートポンプ用吸着剤。

【請求項4】 前記他の金属イオンが K^{+} 又は Ag^{+} の1価の金属イオンからなる請求項1記載のヒートポンプ用吸着剤。

【請求項5】 前記金属置換合成ゼオライトの平均粒子径は0.1~10 μm である請求項1乃至4のいずれかの項に記載のヒートポンプ用吸着剤。

【請求項6】 前記金属置換合成ゼオライトは顆粒状に造粒したものである請求項1乃至5のいずれかの項に記載のヒートポンプ用吸着剤。

【請求項7】 合成ゼオライトは、A型ゼオライト、X型ゼオライト、Y型ゼオライト又はP型ゼオライトから選ばれた少なくとも1種の合成ゼオライトである請求項1乃至6のいずれかの項に記載のヒートポンプ用吸着剤。

【請求項8】 請求項1乃至7のいずれかの項に記載のヒートポンプ用吸着剤を用いることを特徴とするヒートポンプ。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、ヒートポンプ用吸着剤に関し、特に合成ゼオライト中の交換可能な総電荷の33.3%以上を他の金属イオンで置換してなる金属置換合成ゼオライトをヒートポンプ用吸着剤として提供するものである。

【0002】

【従来の技術】 COP3において、我が国は、室温ガス排出量の削減目標を、2012年までに90年レベルの6%減と設定した。その後、既に1990年当時より約15%エネルギー消費が増加しており、目標として掲げた2012年までの残り11年間で20%に及び排出削減を行わなければならない。先進国はそれでも、エネルギー消費の伸びは抑えてきているが、中国などのエネルギー消費は、急上昇している。削減目標は、地球的には達成が困難で、環境の悪化は深刻な事態になる可能性がある。これらの解決方法としては、例えば化石燃料を用いない自然エネルギー等を利用する技術開発を行うことである。これらは、太陽光、熱、風力、温度差発電、核融合など種々の試みがなされている。また、蓄熱などの熱の有効利用などがあ

る。

【0003】 それらに対して1978年、Tchernevにより太陽熱ゼオライトヒートポンプが提唱(D. I. Tchernev, The use of zeolites for solar cooling, Proc. 5th Int. Conf. on Zeolite, Rees, L. B. Sand and F. A. Mumpton eds., Pergamon, Oxford, 479, 1978)され、以後多くのこの種研究がなされている。例えば、ヒートポンプ(特開昭50-103744号公報)、太陽熱を利用のゼオライト製氷冷蔵装置(特開昭59-56068号公報)、ケミカルヒートポンプの熱媒の排気方法(特開昭59-129360号公報)、ケミカルヒートポンプの製造方法(特開昭59-129362号公報)、給湯器(特開昭60-20052号公報)、ケミカルヒートポンプ式給湯器の作動方法(特開昭60-99966号公報)、ケミカルヒートポンプ式給湯器(特開昭60-99967号公報)、ケミカルヒートポンプの駆動方法(特開昭60-126562号公報)、ケミカルヒートポンプ(特開昭60-226674号公報)、低品位の熱源によって作動されるヒートポンプ(特開昭61-502008号公報)、可逆冷熱発生器(特開平1-277180号公報)、ヒートポンプ式空気調和機(特開平2-217729号公報)、吸着式ヒートポンプ(特開平4-225762号公報)、サーモサイフォンを利用した回転モジュール型吸着式ヒートポンプ(特開平4-309760号公報)、吸着式ヒートポンプ(特開平5-322364号公報)、熱の貯蔵及び利用ないし冷気の調製法、並びに吸着装置(特開平5-196318号公報)、化学蓄熱型ヒートポンプ(特開平6-117724号公報)、ヒートポンプ装置(特開平6-331233号公報)、固体吸着体を使用した冷却及び加熱装置(特開平7-120100号公報)、化学的ヒートポンプ用の吸着剤ブロックとその製造方法(特表平7-504360号公報)、ケミカルヒートポンプ(特開平9-152222号公報)、化学蓄熱式吸気冷却装置(特開平10-89798号公報)、蒸気吸放出材料(特開平11-114410号公報)等である。

【0004】 これらに使用されている吸着剤は、ゼオライト、モレキュラーシーブ、セピオライト、シリカゲル、活性炭、吸着性粘土鉱物、活性アルミナ、多孔性炭素繊維、金属多孔体、メソ多孔体などが提案されている。それらの中で、ゼオライト系ヒートポンプが多く開発され提案されている。

【0005】 係るゼオライト-水系ヒートポンプのメリットは、①100~200℃付近の低温の熱源と室温付近の熱源の2つのみで動く。②基本的に電力などの他の熱源が要らない。③蓄熱容量が大きい。④ゼオライトと水という環境問題的に安全で安価な物質で構成できる。⑤蓄熱のための断熱装置が要らない。⑥吸着材として、非晶質物質に比べて、熱膨張性が無く、何度でも繰り返し使用でき、耐久性が高くメンテナンスが簡単であるなどの特徴を有している。

【0006】

【発明が解決しようとする課題】 しかしながら、上記の様にゼオライト-水系ヒートポンプの多くの特徴がある

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にも係わらず未だに実用化されていないのが現状である。今までに実用化に至らなかった理由としては、幾つか考えられるが、その一つはゼオライト水のエントロピー状態やゼオライトの脱水挙動など十分に且つ正しく議論されてこなかったことによると考えられる。従って、前記の開発の殆どがナトリウムタイプのゼオライトのみを使用して研究されているのが現状である。

【0007】本発明者らは、上記問題に鑑み鋭意検討をした結果、ヒートポンプ用吸着剤として、合成ゼオライト中のナトリウムイオンをイオン交換により他の金属イオンで33.3%以上置換してなる金属置換合成ゼオライトをヒートポンプ用として使用することにより極めて効率よく熱交換をすることを発見するに至り、本発明を完成させた。

【0008】

【課題を解決するための手段】すなわち、本発明は、合成ゼオライト中の交換可能な総電荷の33.3%以上を他の金属イオンで置換してなる金属置換合成ゼオライトからなることを特徴とするヒートポンプ用吸着剤に係るものである。

【0009】また、本発明は、他の金属イオンが2価の金属イオンからなる前記のヒートポンプ用吸着剤に係るものである。更にまた、本発明は、2価の金属イオンとしては Mg^{2+} 、 Cu^{2+} 、 Ba^{2+} 、 Sr^{2+} 、 Mn^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ge^{2+} 、 Sn^{2+} 又は Pb^{2+} から選ばれた少なくとも1種の金属イオンである前記のヒートポンプ用吸着剤に係るものである。また、本発明は、他の金属イオンが K^{+} 又は Ag^{+} の1価の金属イオンからなる前記のヒートポンプ用吸着剤に係るものである。

【0010】更にまた、本発明は、金属置換合成ゼオライトの平均粒子径は0.1~10 μm である前記のヒートポンプ用吸着剤に係るものである。また、本発明の金属置換合成ゼオライトは、顆粒状に造粒したものである前記のヒートポンプ用吸着剤に係るものである。更にまた、本発明の合成ゼオライトは、A型ゼオライト、X型ゼオライト、Y型ゼオライト又はP型ゼオライトから選ばれた少なくとも1種の合成ゼオライトである前記のヒートポンプ用吸着剤に係るものである。また、本発明は、前記のヒートポンプ用吸着剤を用いることを特徴とするヒートポンプに係るものである。

【0011】

【発明の実施の形態】以下、本発明を更に詳細に説明する。本発明のヒートポンプ用吸着剤は、合成ゼオライト中の交換可能な総電荷の33.3%以上を他の金属イオンで置換してなる金属置換合成ゼオライトからなることを特徴とするものである。

【0012】係る合成ゼオライトとは、ゼオライト構造を有しそのカチオンが交換可能なものである。このイオン交換前の原体である合成ゼオライトは、例えばA型、

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X型、Y型又はP型ゼオライトが好ましい。その他としてモルデナイト、アナルサイト、ソーダライト、クリノプチロライト、エリオナイト又はチャバサイト等が使用可能である。前記イオン交換前の原体の合成ゼオライトにおいて、カチオンは、ナトリウム、カリウムその他の場合もあるが、通常ナトリウムである。

【0013】本発明に使用するヒートポンプ用吸着剤は、合成ゼオライト中のカチオンであるナトリウムイオンが他の金属イオンとイオン交換された金属置換型ゼオライトを用いている。この交換率は、合成ゼオライト中の交換性の電荷の33.3%以上、好ましくは40%以上としている。

【0014】交換する他の金属イオンとしては、 K^{+} 又は Ag^{+} の1価の金属イオン、又は2価の金属イオンである。交換する2価の金属イオンとしては Mg^{2+} 、 Ca^{2+} 、 Ba^{2+} 、 Sr^{2+} 、 Mn^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ge^{2+} 、 Sn^{2+} 又は Pb^{2+} から選ばれた少なくとも1種の金属イオンである。この中で、 K^{+} 、 Mg^{2+} 、 Co^{2+} が特に好ましい。 Mg^{2+} 、 Co^{2+} が好ましい理由は、後述又は実施例に記載した様に、置換後に含まれる含水量が高いことによる。また、 K^{+} 置換合成ゼオライトは、200~300℃程度の高温でも結晶構造が壊れることなく安定であるため、好ましい。

【0015】合成ゼオライトのイオン交換体は、容易に調製することができる。例えばA型ゼオライトとイオン交換すべき金属の可溶性塩水溶液と充分に接触させることにより得られ、金属塩としては塩化物、硝酸塩、硫酸塩又は有機酸塩等が挙げられる。本発明のヒートポンプ用吸着剤としての金属置換合成ゼオライトは、平均粒子径0.1~20 μm 、好ましくは1~10 μm 、更に好ましくは2~8 μm である。

【0016】これは、金属置換合成ゼオライトの粒径が微細すぎると、真空ポンプでヒートポンプ系内を真空にする際にゼオライトが飛散してしまい好ましくない。また、大粒径のゼオライトにおいては、原体の合成が困難である。以上の理由により、粒径の範囲が決められる。

【0017】また、本発明のヒートポンプ用吸着剤としての金属置換合成ゼオライトは、顆粒状に造粒したものであってもよい。この時の造粒の大きさは、平均で10~100 μm 、好ましくは10~30 μm まで造粒したものである。造粒の方法は、通常工業的に行われている方法でよい。

【0018】次に、ゼオライト-水系ヒートポンプについて説明する。このゼオライト-水系ヒートポンプは使用する合成ゼオライトのNaイオンを他の金属イオンで置換する置換率を高くすることにより、極めて効率のよいヒートポンプを設計することができる。

【0019】ここで、置換率を高くすると、何故ヒートポンプとして使用する場合好ましいかを説明する。合成

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時、A型ゼオライトは $\text{NaAlSi}_3\text{O}_8 \cdot n\text{H}_2\text{O}$ の組成を持っている。このゼオライト結晶構造中の珪酸塩フレームワーク中の空隙には、 Na^+ イオンと H_2O 分子が詰まっている。この水分子の着・脱により熱交換が行われる。この熱交換が、本ヒートポンプシステムの原理である。その場合A型ゼオライトでは、水分子1モルあたり60-67 kJ程度の熱交換（以後、水和エンタルピー、 ΔH 、とする）が可能であり、この値は、交換性陽イオンの種類には余り依存しない。すなわち、熱交換の総量は、空隙内の水分子の数に依存するところが大きい。

【0020】そこで、熱交換を評価するためのQ値（熱交換能）を表現すると、熱交換能Qは下記の式になる。

$$Q = \Delta H_w \times \Delta m_w$$

【式中、Q：熱交換能（kJ/kg（ゼオライト））、 ΔH_w ：水和エンタルピー（kJ/mol（水））、 Δm_w ：水和量（モル（水）/kg（ゼオライト））】

【0021】すなわち、ゼオライト1000gあたりの熱交換容量Qは、ゼオライト中の有効な水分量をW%とすると、

$$Q = \Delta H_w \cdot (W/100) \cdot (1000/18) = 0.55 \cdot \Delta H_w \cdot W \quad (\text{kJ/kg})$$

と与えられる。

【0022】前述の理由から、ヒートポンプ用のゼオライトとしての能力が高いものは、水和エンタルピーの絶対値が大きく、かつ、水の含有量の高いものということが出来る。このとき、水和エンタルピーの値は、組成によっては大きくは変わらないので、ヒートポンプ用のゼオライトの能力は主として含水量に依存する。従って含水量を増やすことが重要である。ゼオライトは、交換性陽イオンを容易に置換できるので、1価の陽イオン（ Na^+ など）を2価の陽イオンで置換すると、陽イオンの数が半分に、水の入る余地を増加させ、含水量を増やすことが出来る。

【0023】3価の陽イオンなど、より多価の陽イオンを導入すればさらに良いはずであるが、一般に3価以上の陽イオンを導入することは困難である。従って、ここにおいては、2価の陽イオン、例えば、 Mg^{2+} 、 Ca^{2+} 、 Ba^{2+} 、 Sr^{2+} 、 Mn^{2+} 、 Co^{2+} 、 Ni^{2+} 、 Cu^{2+} 、 Cd^{2+} 、 Zn^{2+} 、 Ge^{2+} 、 Sn^{2+} 又は Pb^{2+} 等の金属イオンである。この中で、 K^+ 、 Mg^{2+} 、 Co^{2+} が適している。

【0024】このように、陽イオン（金属イオン）の置換率を高くすることにより、よりゼオライト内の水分の含有量を多くさせることができる。このようにして構成する水分量の多いゼオライトをヒートポンプ用吸着剤として用いると、例えば1kg当たりの交換可能な熱量が多くなり、従来にない効率のよいヒートポンプを作成することができるものである。

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【0025】次に、図面を参照して、本発明に係るヒートポンプ（装置）を説明する。図1は本発明の吸着剤を用いたヒートポンプの構成説明図である。ヒートポンプ10は加熱用ヒータ15を設置した水槽11内に複数本のゼオライトベッド13を配設している。そして、ゼオライトベッド13と水受け20とを連絡するパイプ21、および真空ポンプ30に連絡するパイプ23によりヒートポンプ系を形成している。なお、パイプ23途中には真空ゲージ33を配設している。また、符号1から6はパイプ開閉用のコックである。ヒートポンプ10は、金属置換合成ゼオライト粉末をガラス管に充填して、ゼオライトベッド13を形成する。複数のゼオライトベッド13をヒータ15を設置した水槽11に入れ水溜に接続する。まず、真空ポンプ30によりヒートポンプ系内を真空排気する。

【0026】次に、ヒータ15により水槽11内の水を温め、ゼオライトベッド13を湯の中で加熱する。加熱によりゼオライトベッド13内の金属置換合成ゼオライト粉末は脱水する。この時、ゼオライトから脱水した水蒸気は、パイプ21通過途中室温で冷やされて、水受け20の中で凝縮し水として貯えられる。脱水の後、水受け20に連絡するコック2を開き、水槽11の湯を除き、室温の水に取り替え、ゼオライトを室温に冷却する。冷却後、コック2を開くと、超真空状態になっているゼオライトは、水溜まりの水を蒸発させて、吸収し始める。この時、水溜まりの水の上部は急速な蒸発により、蒸発熱を奪われ数分後に凍り始める。それからゆっくり冷えて、過冷却状態になる。そして、-12℃まで冷却したとき、一瞬にして、水溜全体が凍った。

【0027】この実施の形態はヒートポンプ系内を真空排気した場合を示しているが、ヒートポンプ系内は、常圧でもよい。例えば、100℃の低温でゼオライトを脱水する場合は、真空が好ましい。また、160℃の高温でゼオライトを脱水する場合は、ヒートポンプ系内を必ずしも真空にする必要はなく、常圧でもよい。これは、ゼオライトの脱水量に関係があり、低温（100℃以下）で脱水する場合は、ヒートポンプ系内を真空にしなければ、十分な水分量（約15～17wt%）の脱水をすることができないのに対し、高温（160℃）で脱水する場合は、ヒートポンプ系内が必ずしも真空でなくとも十分な水分量（約15～17wt%）の脱水をすることができるからである。

【0028】以上説明した本発明のヒートポンプ用吸着剤並びにこれを用いたヒートポンプは、様々な分野に使用することができる。例えばコンピュータのIC基盤等の冷却、寒冷地の温熱利用、ドライフラワー、低温乾燥、住宅の冷暖房等である。

【0029】（実施例）以下、実施例を示し本発明をさらに具体的に説明する。この実施例における陽イオン交換率（電荷交換率）の測定法は、原子吸光法によりアル

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カリ、アルカリ土類金属、Al、Siを定量分析し、交換を行った金属 M^{n+} および Na^{+} のモル比をそれぞれ m_M 、 m_N 。とすると、陽イオン交換率は $n \times m_M / (n \times m_M + m_N) \times 100 (\%)$ となる。また、含水量の測定方法として、含水量は、熱重量分析(TG)により800℃における脱水率として

求めた。

【0030】実施例1

(1) 合成ゼオライトの化学分析と陽イオン交換率(電荷交換率)、含水量(wt%)を表1に示す。

【表1】

サンプル	化学式	陽イオン交換率(%)	含水量(wt%)
Na-A	$Na_{1.11}(Al_{1.11}Si_{1.11})O_8 \cdot 4.21H_2O$	0	21.65
K-A	$(K_{1.11}Na_{0.11})(Al_{1.11}Si_{1.11})O_8 \cdot 3.84H_2O$	84.79	18.13
Ca-A	$(Ca_{1.11}Na_{0.11})(Al_{1.11}Si_{1.11})O_8 \cdot 4.62H_2O$	89.04	23.46
Mg-A	$(Mg_{1.11}Na_{0.11})(Al_{1.11}Si_{1.11})O_8 \cdot 5.34H_2O$	48.94	26.30
Co-A	$(Co_{1.11}Na_{0.11})(Al_{1.11}Si_{1.11})O_8 \cdot 5.90H_2O$	64.81	27.13

【0031】この結果によると、MgとCoを置換した合成ゼオライト(サンプルMg-A、Co-A)が含水量が高いことが分かる。これは、MgとCoを置換した合成ゼオライトは、大量の水分を含み、ヒートポンプ用吸着剤として使用する場合、高い熱交換能を有することを示している。

【0032】(2) 次いで、表2に表1のサンプルを

大気中(常圧下)で加熱した時の脱水率(wt%)を示す。加熱方法は、上記表1のサンプルを磁製ルツボ中に秤量し、電気炉で昇温して所望温度になったところで、1時間保った後、デシケータ中で放冷しサンプル重量を測定した。

【表2】

サンプル	25~100℃	25~200℃	25~300℃	25~400℃	25~500℃	25~600℃	25~700℃	25~800℃
Na-A	4.23 (wt%)	16.65	19.11	20.66	21.49	21.65	21.66	21.65
K-A	3.21	11.46	16.85	17.87	18.05	18.09	18.12	18.13
Ca-A	4.12	13.90	21.07	21.94	22.45	22.93	23.17	23.46
Mg-A	6.48	20.47	23.52	24.71	25.28	25.68	25.98	26.30
Co-A	8.56	20.44	24.14	25.91	26.50	26.76	26.89	27.13

【0033】この結果より、MgとCoを置換した合成ゼオライト(サンプルMg-A、Co-A)は比較的低温(25~200℃)からの脱水率が高いことが分かる。これは、ヒートポンプ用吸着剤として使用する場合、低温

での加熱で高い熱交換能を持つことを示している。

【0034】(3) 脱水温度毎のQ値(熱交換能)の関係を表3に示す。

【表3】

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脱 水 温	40	60	80	100	120	140	160	180
度								
$\theta d/^{\circ}\text{C}$	$Qa/\text{kJ}\cdot\text{kg}^{-1}$							
Na-A	137	179	279	505	621	669	665	662
K-A	92	155	226	302	509	599	674	678
Ca-A	133	212	288	371	486	614	718	789
Mg-A	161	394	517	690	759	805	838	865
Co-A	219	350	521	630	685	748	826	864

【0035】また、上記関係を図2のグラフに示している。なお、サンプルK-Aは熱安定性が良いので350℃までのデータを示している。

【0036】実施例2 (Mg置換合成ゼオライトの置換率による含水率の特性測定)

Na-A型合成ゼオライトを、Mgイオンで置換した。その結果を表4に示す。脱水温度は100℃で、1時間ロータリーポンプで真空引きして行った。

【表4】

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試料	置換率	試料重量	脱水量	水和量	水和 ΔH	水和熱	完全水	水和開	温度変	含水率
(単位)	%	W(g)	Wd(X)	Wh(X)	- ΔH (kJ/mol)	Q(kJ/kg)	Q'(kJ/kg)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	(wt%)
M-1	37.73	0.24826	18.34	16.27	65.61	592.83	888.44	17.13	0.085128	24.69
M-2	41.38	0.25423	18.01	16.95	64.64	608.84	850.09	17.94	0.089568	25.54
M-3	41.84	0.25155	17.75	16.72	64.09	595.36	832.02	16.26	0.088495	25.45
M-4	44.24	0.24760	17.99	16.81	64.51	602.60	844.85	16.69	0.087379	25.61
M-5	47.58	0.26114	17.07	14.90	67.41	557.98	839.15	16.62	0.085529	25.88
M-6	52.56	0.28059	16.01	13.62	65.35	494.48	581.29	17.61	0.075874	26.74
M-7	54.74	0.26495	16.81	15.55	64.61	568.18	603.29	17.46	0.086733	26.48
M-8	65.21	0.26427	17.14	15.34	65.85	561.05	626.94	16.97	0.086069	26.51
M-9	67.85	0.26096	17.57	15.42	65.73	563.20	641.69	17.38	0.089161	26.88

【0037】これによると、Mg置換37.73%合成ゼオライトに対し、Mg置換67.85%合成ゼオライトの含水率（水分量）の差は、2.19wt%である。さらに、水の全量との比率にすると8.1wt%の増加となり、Mgの置換が多いほど、高い熱交換能を有することがわかる。

【0038】実施例3

実施例1のMg置換A型ゼオライト（サンプル名：Mg-A）（日本化学工業（株）製、商品名「ゼオスターGA-100P」）350gを6本の外径3cmのガラス管（13）に入れ、水が入っている水槽（11）に接続した。・・・図1参照

【0039】次いで、ヒートポンプ系内を真空排気し、真空状態をゲージ33で確認した。次いで、水槽11のヒータ15で約100℃まで加熱した。この時、ガラス管内のゼオライトは脱水され、ゼオライトから脱水した水蒸気は、パイプ21通過途上室温で冷やされ、水受け 50

20中で凝縮し水として貯えられる。脱水の後、コック2を閉じ、水槽11の湯を除き、室温の水に取り替える。脱水されたMg置換A型ゼオライトは室温まで冷却される。

【0040】冷却後、コック2を開くと、真空状態になっているゼオライトは、水溜まりの水を蒸発させて、吸収し始める。この時、水溜まりの水の上部は急速な蒸発により、蒸発熱を奪われ数分後に凍り始める。ゆっくり冷えて、過冷却状態になり、-12℃になって一瞬にして、水滴全体が凍った。

【0041】実施例4～6

実施例3のMg置換A型ゼオライト（サンプル名：Mg-A）の代わりに下記表5の金属置換合成ゼオライトを使用した他は、実施例3と同様に行った結果、実施例3と同様に水を凍らせることができた。

【表5】

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	サンプル
実施例 4	K-A
実施例 5	Ca-A
実施例 6	Co-A

【0042】比較例1

実施例2のMg置換A型ゼオライト(サンプル名:Mg-A)の代わりに実施例1の表1に示されているサンプルNa-Aを使用して、実施例3と同様の実験を行った。その結果、水を凍らせるのに非常に時間がかかり、効率が悪いことがわかった。

【0043】

【発明の効果】以上説明したように、本発明のヒートポンプ用吸着剤は、合成ゼオライトを金属置換したものであるが、ゼオライト中に含まれる含水量が多いため、その水和エンタルピーの絶対値が大きく、熱交換能が極めて高い。よって、従来無い効率の高いヒートポンプを作ることができる。これにより、本発明のヒートポンプ用吸着剤を用いれば、広い分野でヒートポンプを実際

に使用することが可能となり、エネルギー資源の節約に寄与することができる。

【図面の簡単な説明】

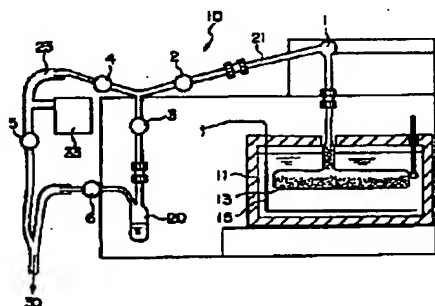
【図1】ヒートポンプの構成説明図。

【図2】脱水温度と熱交換能との関係を示すグラフ。

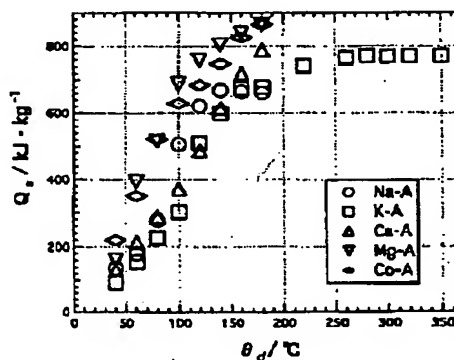
【符号の説明】

- 1, 2, 3, 4, 5, 6 コック
10 ヒートポンプ
11 水槽
13 ゼオライトベッド
16 ヒータ
20 水受け
30 真空ポンプ
33 真空ゲージ

【図1】



【図2】



フロントページの続き

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Fターム(参考) 3L093 NN04 RR03

4G066 AA62B BA09 BA20 CA43

EA20 FA26 GA01

4G073 BA05 BA10 BA11 BA12 BA13

BA32 BA40 BA44 BA48 BA49

BA52 BA53 BA64 BA65 BA66

BD21 CZ02 CZ04 CZ05 CZ26

FD08 FD26 GA11 GA39 UA06

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-239156

(43)Date of publication of application : 04.09.2001

(51)Int.Cl.

B01J 20/18

C01B 39/02

F25B 17/08

(21)Application number : 2000-056253

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(22)Date of filing : 01.03.2000

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(54) ADSORBENT FOR HEAT PUMP AND HEAT PUMP USING ADSORBENT

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain an adsorbent for a heat pump which does heat exchange efficiently by the use of synthetic zeolite.

SOLUTION: The adsorbent comprises metal-substituted synthetic zeolite in which at least 33.3% of the total replaceable charge of the synthetic zeolite is replaced with other metal ions. The substituent divalent metal ions are one or more kinds of metal ions, for example, selected from Mg²⁺, Ca²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Co²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Zn²⁺, Ge²⁺, Sn²⁺, and Pb²⁺, or univalent metal ions of K⁺ or Ag⁺.

LEGAL STATUS

[Date of request for examination]

23.06.2004

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the
examiner's decision of rejection or application converted
registration]

[Date of final disposal for application]

[Patent number].

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of
rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The adsorbent for heat pump characterized by consisting of metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge in permutite 33.3% or more.

[Claim 2] The adsorbent for heat pump according to claim 1 with which a metal ion besides the above consists of a divalent metal ion.

[Claim 3] The adsorbent for heat pump according to claim 2 which are at least one sort of metal ions with which said divalent metal ion was chosen from Mg^{2+} , $calcium^{2+}$, Ba^{2+} , Sr^{2+} , Mn^{2+} , Co^{2+} , $nickel^{2+}$, Cu^{2+} , Cd^{2+} , Zn^{2+} , $germanium^{2+}$, Sn^{2+} , or Pb^{2+} .

[Claim 4] said — others — the adsorbent for heat pump according to claim 1 with which a metal ion consists of a univalent metal ion of K^{+} or Ag^{+} .

[Claim 5] The mean particle diameter of said metal replacement permutite is an adsorbent for heat pump given in claim 1 which is 0.1–10 micrometers thru/or one term of 4.

[Claim 6] Said metal replacement permutite is an adsorbent for heat pump given in claim 1 which comes to granularity thru/or one term of 5.

[Claim 7] Permutite is an adsorbent for heat pump given in claim 1 which are at least one sort of permutite chosen from A mold zeolite, the X type zeolite, Y mold zeolite, or the P type zeolite thru/or one term of 6.

[Claim 8] Heat pump characterized by using the adsorbent for heat pump of a publication for claim 1 thru/or one term of 7.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention offers the metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge especially in permutite 33.3% or more as an adsorbent for heat pump about the adsorbent for heat pump.

[0002]

[Description of the Prior Art] In COP3, our country set up the reduction target of a room temperature gas discharge with a 6% decrease of 90-year level by 2012. Then, energy expenditure has increased already from that time about 15% in 1990, and discharge reduction which reaches to 20% before [remaining 11 years] 2012 hung up as a target must be performed. Although advanced nations have still been suppressing the elongation of energy expenditure, energy expenditure, such as China, is going abruptly up. A reduction target may be terrestrially difficult to attain and environmental aggravation may become a serious situation. It is performing ED which uses the natural energy which does not use a fossil fuel, for example as these solution approaches. As for these, various attempts, such as sunlight, heat, a wind force, an electric generation by temperature difference, and nuclear fusion, are made. Moreover, there is a deployment of heat, such as accumulation, etc.

[0003] Solar-heat zeolite heat pump will be advocated by Tchernev to them in 1978 (D. 479 I.Tchernev, The use of zeolites for solar cooling, Proc. 5th Int. Conf. on Zeolite, Rees, L.B. Sand and F.A. Mumpton eds., Pergamon, Oxford, 1978), many of these seed researches are made henceforth, and it is. For example, heat pump (JP,50-103744,A), zeolite ice-making refrigeration equipment of use of solar heat (JP,59-56068,A), The exhaust air approach of the heat carrier of chemical heat pump (JP,59-129360,A), The manufacture approach of chemical heat pump (JP,59-129362,A), The actuation approach of a hot-water supply machine (JP,60-20052,A) and a chemical-heat-pump type hot-water supply machine (JP,60-99966,A), A chemical-heat-pump type hot-water supply machine (JP,60-99967,A), The drive approach of chemical heat pump (JP,60-126562,A), Chemical heat pump (JP,60-226674,A), the heat pump which operates according to the heat source of low grade (JP,61-502008,A), An reversible cold energy generator (JP,1-277180,A), a heat pump type air conditioner (JP,2-217729,A), Adsorption equation heat pump (JP,4-225762,A), the rotation module mold adsorption equation heat pump using a thermostat siphon (JP,4-309760,A), The method of preparation of the storage and use thru/or cold of adsorption equation heat pump (JP,5-322364,A) and heat, In a list, an adsorber (JP,5-196318,A), chemico-thermal-storage mold heat pump (JP,6-117724,A), Cooling and heating apparatus (JP,7-120100,A) which used heat pump equipment (JP,6-331233,A) and a solid-state absorber, The adsorbent block and its manufacture approach (Patent Publication Heisei No. 504360 [seven to] official report) for chemical heat pump, They are chemical heat pump (JP,9-152222,A), a chemico-thermal-storage type inhalation-of-air cooling system (JP,10-89798,A), a steamy absorption/emission ingredient (JP,11-114410,A), etc.

[0004] As for the adsorbent currently used for these, a zeolite, a molecular sieve, sepiolite, silica gel, activated carbon, an adsorbent clay mineral, the activated alumina, the porous carbon fiber, the metal porous body, the meso porous body, etc. are proposed. In them, many zeolite system heat pump is developed and is proposed.

[0005] The merit of the zeolite-drainage system heat pump to apply moves only by two, the heat source of the low temperature near **100-200 degree C, and the heat source near a room temperature. ** Other heat sources, such as power, are not needed fundamentally. ** Accumulation capacity is large. ** It can constitute from matter safe in environmental problem, and cheap called a zeolite and water. ** The heat insulation equipment for accumulation is not needed. ** as adsorption material, compared with the amorphous matter, there is no thermal-expansion nature, it can be used repeatedly any number of times, and a maintenance is [endurance is high and] easy — etc. — it has the description.

[0006]

[Problem(s) to be Solved by the Invention] However, the present condition is not yet put in practical use although there are many descriptions of zeolite-drainage system heat pump as mentioned above. although some are considered as a reason which did not result in utilization until now — one of them — the entropy condition of zeolite water, the dehydration behavior of a zeolite, etc. — enough — and it is thought that it is because it did not argue correctly.

Therefore, the present condition is that most development of the above is studied only using a sodium type zeolite.

[0007] As a result of inquiring wholeheartedly in view of the above-mentioned problem, by using the metal replacement permutite which comes to permute the sodium ion in permutite with other metal ions according to the ion exchange 33.3% or more as an object for heat pump as an adsorbent for heat pump, this invention persons came to do the knowledge of carrying out heat exchange very efficiently, and completed this invention.

[0008]

[Means for Solving the Problem] That is, this invention relates to the adsorbent for heat pump characterized by consisting of metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge in permutite 33.3% or more.

[0009] Moreover, this invention relates to the aforementioned adsorbent for heat pump with which other metal ions consist of a divalent metal ion. Furthermore, this invention relates to the aforementioned adsorbent for heat pump which are at least one sort of metal ions chosen from Mg²⁺, calcium²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Co²⁺, nickel²⁺, Cu²⁺, Cd²⁺, Zn²⁺, germanium²⁺, Sn²⁺, or Pb²⁺ as a divalent metal ion again. Moreover, this invention relates to the aforementioned adsorbent for heat pump with which other metal ions consist of a univalent metal ion of K⁺ or Ag⁺.

[0010] Furthermore, the mean particle diameter of metal replacement permutite is applied to the aforementioned

adsorbent for heat pump which is 0.1–10 micrometers by this invention again. Moreover, the metal replacement permutite of this invention is applied to the aforementioned adsorbent for heat pump which comes to granularity. Furthermore, the permutite of this invention is applied to the aforementioned adsorbent for heat pump which are at least one sort of permutite chosen from A mold zeolite, the X type zeolite, Y mold zeolite, or the P type zeolite again. Moreover, this invention relates to the heat pump characterized by using the aforementioned adsorbent for heat pump. [0011]

[Embodiment of the Invention] Hereafter, this invention is further explained to a detail. The adsorbent for heat pump of this invention is characterized by consisting of metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge in permutite 33.3% or more.

[0012] The permutite to apply has the exchangeable cation of owner *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. in zeolite structure. The permutite which is a original object in front of this ion exchange has A mold, an X type, Y mold, or a desirable P type zeolite. Mordenite, ANARUSAIMU, a soda light, clinoptilolite, erionite, or a CHABA site is usable as others. In the permutite of the original object in front of said ion exchange, a cation is usually sodium, although there is also a case of sodium, a potassium, and others.

[0013] The metal replacement mold zeolite with which the ion exchange of the sodium ion which is a cation in permutite was carried out to other metal ions is used for the adsorbent for heat pump used for this invention. this rate of exchange — the charge of the convertibility in permutite — it may be 40% or more preferably 33.3% or more.

[0014] As other metal ions to exchange, they are the univalent metal ion of K⁺ or Ag⁺, or a divalent metal ion. They are at least one sort of metal ions chosen from Mg²⁺, calcium²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Co²⁺, nickel²⁺, Cu²⁺, Cd²⁺, Zn²⁺, germanium²⁺, Sn²⁺, or Pb²⁺ as a divalent metal ion to exchange. In this, K⁺, Mg²⁺, and especially Co²⁺ are desirable. It is because the moisture content whose Mg²⁺ and Co²⁺ indicated the desirable reason in the after-mentioned or the example and which is contained after a permutation is [like] high. Moreover, without the crystal structure breaking, since it is stable, even an about 200–300-degree C elevated temperature is desirable [K⁺ permutation permutite].

[0015] The ion exchanger of permutite can be prepared easily. For example, it is obtained by making the fusibility salt water solution of the metal which should be carried out the ion exchange to A mold zeolite fully contact. As a metal salt, a chloride, a nitrate, a sulfate, or an organic-acid salt is mentioned. 1–10 micrometers of metal replacement permutite as an adsorbent for heat pump of this invention are 2–8 micrometers still more preferably preferably the mean particle diameter of 0.1–20 micrometers.

[0016] If the particle size of metal replacement permutite is too detailed, a zeolite disperses and is not desirable [this] in case this makes the inside of a heat pump system a vacuum with a vacuum pump. Moreover, in the zeolite of the diameter of a large drop, composition of a original object is difficult. The range of particle size is decided for the above reason.

[0017] Moreover, you may corn the metal replacement permutite as an adsorbent for heat pump of this invention to granularity. The magnitude of the granulation at this time is preferably corned to 10–30 micrometers 10–100 micrometers on an average. The approach of a granulation is good by the approach usually performed industrially.

[0018] Next, zeolite-drainage system heat pump is explained. By making high the substitutional rate which permutes Na ion of the permutite to be used with other metal ions, this zeolite-drainage system heat pump can design very efficient heat pump.

[0019] Here, if a substitutional rate is made high, it will explain why it is desirable when using it as heat pump. A mold zeolite has the presentation of NaAlSiO₈ and nH₂O at the time of composition. Na ion and an H₂O molecule are got blocked in the opening in the silicate framework in this zeolite crystal structure. This water molecule wears and heat exchange is performed by — **. This heat exchange is the principle of this heat pump system. In that case, in A mold zeolite, the heat exchange (henceforth referred to as hydration enthalpy and deltaH) of 60–67kJ extent is possible per one mol of water molecules, and it seldom depends for this value on the class of convertibility cation. That is, the total amount of heat exchange has a large place depending on the number of the water molecules in an opening.

[0020] Then, if the Q value (heat exchange ability) for evaluating heat exchange is expressed, the heat exchange ability Q will become the following formula.

$Q = \Delta H \times \Delta m_h$ [inside of formula, Q: heat exchange ability (kJ/kg (zeolite)), and ΔH : hydration enthalpy (kJ/mol(water)), and the amount of Δm_h : hydration (a mol(water)/kg (zeolite))]

[0021] That is, the heat exchange capacity Q per zeolite 1000g is $Q = \Delta H - (W/100) - (1000/18) = 0.55$ and $\Delta H - W$, when the effective moisture content in a zeolite is made into W %. (kJ/kg)

It is given.

[0022] From the above-mentioned reason, the absolute value of hydration enthalpy can call greatly what has the high capacity as a zeolite for heat pump what has the high content of water. Since the value of hydration enthalpy does not change a lot depending on a presentation at this time, it mainly depends for the capacity of the zeolite for heat pump on moisture content. Therefore, rising is important. Since a zeolite can permute a convertibility cation easily, if a divalent cation permutes univalent cations (Na etc.), the number of cations can become half, and it can make the room of water to enter able to increase, and can rise.

[0023] Although it must be still better if a trivalent cation etc. introduces the cation of many ** more, it is difficult to introduce the cation more than trivalent generally. Therefore, in here, they are metal ions, such as a divalent cation, for example, Mg²⁺, calcium²⁺, Ba²⁺, Sr²⁺, Mn²⁺, Co²⁺, nickel²⁺, Cu²⁺, Cd²⁺, Zn²⁺, germanium²⁺, Sn²⁺, or Pb²⁺. In this, K⁺, Mg²⁺, and Co²⁺ are suitable.

[0024] Thus, the content of the moisture in a zeolite can be made [many] more by making the substitutional rate of a cation (metal ion) high. Thus, if a zeolite with many moisture contents to constitute is used as an adsorbent for heat pump, the exchangeable heating value per kg increases, for example, and heat pump with the sufficient effectiveness which is not in the former can be created.

[0025] Next, with reference to a drawing, the heat pump (equipment) concerning this invention is explained. Drawing 1 is the configuration explanatory view of the heat pump which used the adsorbent of this invention. Heat pump 10 is arranging two or more zeolite beds 13 in the tank 11 which installed the heater 15 for heating. And the heat pump system is formed with the pipe 21 which connects the zeolite bed 13 and the water receptacle 20, and the pipe 23 connected to a vacuum pump 30. In addition, the vacuum gage 33 is arranged in pipe 23 way. Moreover, signs 1–6 are the cocks for pipe closing motion. Heat pump 10 fills up a glass tube with metal replacement permutite powder, and forms zeolite ** DDO 13. Two or more zeolite ** DDO 13 is put into the tank 11 which installed the heater 15, and it connects with a sump. First, evacuation of the inside of a heat pump system is carried out with a vacuum pump 30.

[0026] Next, at a heater 15, being [no tank 11] water is warmed and the zeolite bed 13 is heated in a molten bath. The metal replacement permutite powder in the zeolite bed 13 is dehydrated with heating. At this time, the steam dehydrated from the zeolite is cooled at a pipe 21 passage way room temperature, is condensed in the water receptacle 20, and is stored as water. The cock 2 who connects with the water receptacle 20 is closed after dehydration, it exchanges in the water of a room temperature except for the molten bath of a tank 11, and a zeolite is cooled to a room temperature. If a cock 2 is opened, the zeolite which is a super-vacua will evaporate the water of a puddle, and it is begun to absorb it after cooling. At this time, evaporation heat is taken by rapid evaporation and the upper part of the water of a puddle begins to freeze after several minutes. It gets cold slowly and will be in a supercooling condition from it. And when it cooled to -12 degrees C, the whole sump froze in an instant.

[0027] Although the case where the gestalt of this operation carries out evacuation of the inside of a heat pump system is shown, ordinary pressure is sufficient as the inside of a heat pump system. For example, a vacuum is desirable when dehydrating a zeolite at 100-degree C low temperature. Moreover, when dehydrating a zeolite at a 160-degree C elevated temperature, it is not necessary to necessarily make the inside of a heat pump system into a vacuum, and ordinary pressure is sufficient. When this is related to the amount of dehydration of a zeolite and it dehydrates at low temperature (100 degrees C or less) If the inside of a heat pump system is not made into a vacuum, when dehydrating at an elevated temperature (160 degrees C) to the ability not to dehydrate sufficient moisture content (about 15 to 17 wt%) It is because sufficient moisture content (about 15 to 17 wt%) can be dehydrated even if the inside of a heat pump system is not necessarily a vacuum.

[0028] The heat pump which used this for the adsorbent list for heat pump of this invention explained above can be used for various fields. For example, it is the air conditioning of cooling of IC base of a computer etc., warm temperature use of a cold district, a dried flower, low-temperature desiccation, and a residence etc.

[0029] (Example) Hereafter, an example is shown and this invention is explained still more concretely. When the measuring method of the rate of the cation exchange in this example (rate of charge exchange) carries out quantitative analysis of alkali, alkaline earth metal, and aluminum and Si with an atomic absorption method and the mole ratio of exchanged metal Mn^{+} and Na^{+} is set to $mMmNa$, respectively, the rate of the cation exchange is $nxmM/(nxmM+mNa) \times 100 (\%)$.

It becomes. Moreover, moisture content was calculated as a rate of dehydration in 800 degrees C by thermogravimetric analysis (TG) as a measuring method of moisture content.

[0030] Example 1 (1) The chemical analysis of permutite, the rate of the cation exchange (rate of charge exchange); and moisture content (wt%) are shown in Table 1.

[Table 1]

サンプル	化学式	陽イオン交換率(%)	含水量(wt%)
Na-A	$Na_{1.15}(Al_{1.14} \cdot Si_{1.01})O_3 \cdot 4.21H_2O$	0	21.65
K-A	$(K_{1.12} \cdot Na_{0.22})(Al_{1.15} \cdot Si_{1.01})O_3 \cdot 3.84H_2O$	84.79	18.13
Ca-A	$(Ca_{0.11} \cdot Na_{0.11})(Al_{1.03} \cdot Si_{1.15})O_3 \cdot 4.62H_2O$	89.04	23.46
Mg-A	$(Mg_{0.13} \cdot Na_{1.01})(Al_{1.14} \cdot Si_{1.01})O_3 \cdot 5.34H_2O$	48.94	26.30
Co-A	$(Co_{0.11} \cdot Na_{0.11})(Al_{1.14} \cdot Si_{1.01})O_3 \cdot 5.90H_2O$	64.81	27.13

[0031] According to this result, it turns out that the permutite (sample Mg-A, Co-A) which permuted Mg and Co has high moisture content. This and the permutite which permuted Mg and Co show that it has high heat exchange ability, when using it as an adsorbent for heat pump including a lot of moisture.

[0032] (2) Subsequently, the rate of dehydration (wt%) when heating the sample of Table 1 in atmospheric air (under ordinary pressure) is shown in Table 2. After maintaining the heating approach for 1 hour, it was cooled radiationally in the desiccator and measured sample weight in the place which carried out weighing capacity of the sample of the above-mentioned table 1 into the porcelain crucible, carried out the temperature up with the electric furnace, and became request temperature.

[Table 2]

サンプル	25~100 ℃	25~200 ℃	25~300 ℃	25~400 ℃	25~500 ℃	25~600 ℃	25~700 ℃	25~800 ℃
Na-A	4.23 (wt%)	16.65	19.11	20.66	21.49	21.65	21.66	21.65
K-A	3.21	11.46	16.85	17.87	18.05	18.09	18.12	18.13
Ca-A	4.12	13.90	21.07	21.94	22.45	22.93	23.17	23.46
Mg-A	6.48	20.47	23.52	24.71	25.26	25.68	25.98	26.30
Co-A	8.56	20.44	24.14	25.91	26.50	26.76	26.99	27.13

[0033] From this result, the permutite (sample Mg-A, Co-A) which permuted Mg and Co is understood that the rate of dehydration from low temperature (25-200 degrees C) is comparatively high. This shows that it has high heat exchange

ability with heating at low temperature, when using it as an adsorbent for heat pump.

[0034] (3) The relation of the Q value (heat exchange ability) for every dehydration temperature is shown in Table 3.

[Table 3]

脱水温度	40	60	80	100	120	140	160	180
$\theta d/^{\circ}\text{C}$	$Q_s/\text{kJ} \cdot \text{kg}^{-1}$							
Na-A	137	179	279	505	621	669	665	662
K-A	92	155	226	302	509	599	674	678
Ca-A	133	212	288	371	486	614	718	789
Mg-A	161	394	517	690	759	805	838	865
Co-A	219	350	521	630	685	748	826	864

[0035] Moreover, the above-mentioned relation is shown in the graph of drawing 2. In addition, since sample K-A has good thermal stability, the data to 350 degrees C are shown.

[0036] Example 2 (property measurement of the water content by the substitutional rate of Mg permutite) Mg ion permuted the Na-A type composition zeolite. The result is shown in Table 4. Dehydration temperature was 100 degrees C, and vacuum suction of it was carried out with the rotary pump for 1 hour, and it was performed.

[Table 4]

試料	置換率	試料重量	脱水量	水和量	水和1% 外比	水和熱 量	完全水 和熱量	水和開 始温度	温度変 化	含水率
(単位)	%	W(g)	Wd(%)	Wh(%)	- Δ H(kJ/mol)	Q(kJ/kg)	Q'(kJ/kg)	($^{\circ}\text{C}$)	($^{\circ}\text{C}$)	(wt%)
M-1	37.73	0.24826	18.34	16.27	65.61	592.83	668.44	17.13	0.085126	24.69
M-2	41.38	0.25423	18.01	16.95	64.64	608.84	650.09	17.94	0.089568	25.54
M-3	41.84	0.25155	17.75	16.72	64.09	595.36	632.02	16.26	0.088495	25.45
M-4	44.24	0.24760	17.99	16.81	64.51	602.60	644.85	15.69	0.087379	25.61
M-5	47.58	0.26114	17.07	14.90	67.41	557.98	639.15	16.62	0.085529	25.88
M-6	52.56	0.26059	16.01	13.62	65.35	494.48	581.29	17.61	0.075674	26.74
M-7	64.74	0.26495	16.81	15.55	64.61	558.18	603.29	17.46	0.086733	26.48
M-8	65.21	0.26427	17.14	15.34	65.85	561.05	626.94	16.97	0.086069	26.51
M-9	67.85	0.2609	17.57	15.42	65.73	563.20	641.69	17.38	0.0891	26.88

[Table 5]

	サンプル
実施例 4	K-A
実施例 5	Ca-A
実施例 6	Co-A

[Effect of the Invention] As explained above, although it carries out metal replacement of the permutite, since the adsorbent for heat pump of this invention has much moisture content contained in a zeolite, its absolute value of the hydration enthalpy is large, and heat exchange ability is very high [an adsorbent]. Therefore, heat pump with the high effectiveness which is not conventionally can be created. Thereby, if the adsorbent for heat pump of this invention is used, it becomes possible to actually use heat pump in a large field, and can contribute to saving of an energy resource.

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TECHNICAL FIELD

[Field of the Invention] This invention offers the metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge especially in permutite 33.3% or more as an adsorbent for heat pump about the adsorbent for heat pump.

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PRIOR ART

[Description of the Prior Art] In COP3, our country set up the reduction target of a room temperature gas discharge with a 6% decrease of 90-year level by 2012. Then, energy expenditure has increased already from that time about 15% in 1990, and discharge reduction which reaches to 20% before [remaining 11 years] 2012 hung up as a target must be performed. Although advanced nations have still been suppressing the elongation of energy expenditure, energy expenditure, such as China, is going abruptly up. A reduction target may be terrestrially difficult to attain and environmental aggravation may become a serious situation. It is performing ED which uses the natural energy which does not use a fossil fuel, for example as these solution approaches. As for these, various attempts, such as sunlight, heat, a wind force, an electric generation by temperature difference, and nuclear fusion, are made. Moreover, there is a deployment of heat, such as accumulation, etc.

[0003] Solar-heat zeolite heat pump will be advocated by Tchernev to them in 1978 (D. 479 I.Tchernev, The use of zeolites for solar cooling, Proc.5th Int.Conf.on Zeolite, Rees, L.B.Sand and F.A.Mumpton eds., Pergamon, Oxford, 1978), many of these seed researches are made henceforth, and it is. For example, heat pump (JP,50-103744,A), zeolite ice-making refrigeration equipment of use of solar heat (JP,59-56068,A), The exhaust air approach of the heat carrier of chemical heat pump (JP,59-129360,A), The manufacture approach of chemical heat pump (JP,59-129362,A), The actuation approach of a hot-water supply machine (JP,60-20052,A) and a chemical-heat-pump type hot-water supply machine (JP,60-99966,A), A chemical-heat-pump type hot-water supply machine (JP,60-99967,A), The drive approach of chemical heat pump (JP,60-126562,A), Chemical heat pump (JP,60-226674,A), the heat pump which operates according to the heat source of low grade (JP,61-502008,A), An reversible cold energy generator (JP,1-277180,A), a heat pump type air conditioner (JP,2-217729,A), Adsorption equation heat pump (JP,4-225762,A), the rotation module mold adsorption equation heat pump using a thermostat siphon (JP,4-309760,A), The method of preparation of the storage and use thru/or cold of adsorption equation heat pump (JP,5-322364,A) and heat, In a list, an adsorber (JP,5-196318,A), chemico-thermal-storage mold heat pump (JP,6-117724,A), Cooling and heating apparatus (JP,7-120100,A) which used heat pump equipment (JP,6-331233,A) and a solid-state absorber, The adsorbent block and its manufacture approach (Patent Publication Heisei No. 504360 [seven to] official report) for chemical heat pump, They are chemical heat pump (JP,9-152222,A), a chemico-thermal-storage type inhalation-of-air cooling system (JP,10-89798,A), a steamy absorption/emission ingredient (JP,11-114410,A), etc.

[0004] As for the adsorbent currently used for these, a zeolite, a molecular sieve, sepiolite, silica gel, activated carbon, an adsorbent clay mineral, the activated alumina, the porous carbon fiber, the metal porous body, the meso porous body, etc. are proposed. In them, many zeolite system heat pump is developed and is proposed.

[0005] The merit of the zeolite-drainage system heat pump to apply moves only by two, the heat source of the low temperature near **100-200 degree C, and the heat source near a room temperature. ** Other heat sources, such as power, are not needed fundamentally. ** Accumulation capacity is large. ** It can constitute from matter safe in environmental problem, and cheap called a zeolite and water. ** The heat insulation equipment for accumulation is not needed. ** as adsorption material, compared with the amorphous matter, there is no thermal-expansion nature, it can be used repeatedly any number of times, and a maintenance is [endurance is high and] easy — etc. — it has the description.

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EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, although it carries out metal replacement of the permutite, since the adsorbent for heat pump of this invention has much moisture content contained in a zeolite, its absolute value of the hydration enthalpy is large, and heat exchange ability is very high [an adsorbent]. Therefore, heat pump with the high effectiveness which is not conventionally can be created. Thereby, if the adsorbent for heat pump of this invention is used, it becomes possible to actually use heat pump in a large field, and can contribute to saving of an energy resource.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, the present condition is not yet put in practical use although there are many descriptions of zeolite-drainage system heat pump as mentioned above. although some are considered as a reason which did not result in utilization until now — one of them — the entropy condition of zeolite water, the dehydration behavior of a zeolite, etc. — enough — and it is thought that it is because it did not argue correctly. Therefore, the present condition is that most development of the above is studied only using a sodium type zeolite. [0007] As a result of inquiring wholeheartedly in view of the above-mentioned problem, by using the metal replacement permutite which comes to permute the sodium ion in permutite with other metal ions according to the ion exchange 33.3% or more as an object for heat pump as an adsorbent for heat pump, this invention persons came to do the knowledge of carrying out heat exchange very efficiently, and completed this invention.

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MEANS

[Means for Solving the Problem] That is, this invention relates to the adsorbent for heat pump characterized by consisting of metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge in permutite 33.3% or more.

[0009] Moreover, this invention relates to the aforementioned adsorbent for heat pump with which other metal ions consist of a divalent metal ion. Furthermore, this invention relates to the aforementioned adsorbent for heat pump which are at least one sort of metal ions chosen from Mg^{2+} , calcium $^{2+}$, Ba^{2+} , Sr^{2+} , Mn^{2+} , Co^{2+} , nickel $^{2+}$, Cu^{2+} , Cd^{2+} , Zn^{2+} , germanium $^{2+}$, Sn^{2+} , or Pb^{2+} as a divalent metal ion again. Moreover, this invention relates to the aforementioned adsorbent for heat pump with which other metal ions consist of a univalent metal ion of K^{+} or Ag^{+} .

[0010] Furthermore, the mean particle diameter of metal replacement permutite is applied to the aforementioned adsorbent for heat pump which is 0.1–10 micrometers by this invention again. Moreover, the metal replacement permutite of this invention is applied to the aforementioned adsorbent for heat pump which comes to granularity. Furthermore, the permutite of this invention is applied to the aforementioned adsorbent for heat pump which are at least one sort of permutite chosen from A mold zeolite, the X type zeolite, Y mold zeolite, or the P type zeolite again. Moreover, this invention relates to the heat pump characterized by using the aforementioned adsorbent for heat pump.

[0011]

[Embodiment of the Invention] Hereafter, this invention is further explained to a detail. The adsorbent for heat pump of this invention is characterized by consisting of metal replacement permutite which it comes to permute with the metal ion of everything but the exchangeable net charge in permutite 33.3% or more.

[0012] The permutite to apply has the exchangeable cation of owner *Perilla frutescens* (L.) Britton var. *crispa* (Thunb.) Decne. in zeolite structure. The permutite which is a original object in front of this ion exchange has A mold, an X type, Y mold, or a desirable P type zeolite. Mordenite, ANARUSAIMU, a soda light, clinoptilolite, erionite, or a CHABA site is usable as others. In the permutite of the original object in front of said ion exchange, a cation is usually sodium, although there is also a case of sodium, a potassium, and others.

[0013] The metal replacement mold zeolite with which the ion exchange of the sodium ion which is a cation in permutite was carried out to other metal ions is used for the adsorbent for heat pump used for this invention. this rate of exchange — the charge of the convertibility in permutite — it may be 40% or more preferably 33.3% or more.

[0014] As other metal ions to exchange, they are the univalent metal ion of K^{+} or Ag^{+} , or a divalent metal ion. They are at least one sort of metal ions chosen from Mg^{2+} , calcium $^{2+}$, Ba^{2+} , Sr^{2+} , Mn^{2+} , Co^{2+} , nickel $^{2+}$, Cu^{2+} , Cd^{2+} , Zn^{2+} , germanium $^{2+}$, Sn^{2+} , or Pb^{2+} as a divalent metal ion to exchange. In this, K^{+} , Mg^{2+} , and especially Co^{2+} are desirable. It is because the moisture content whose Mg^{2+} and Co^{2+} indicated the desirable reason in the after-mentioned or the example and which is contained after a permutation is [like] high. Moreover, without the crystal structure breaking, since it is stable, even an about 200–300-degree C elevated temperature is desirable [K^{+} permutation permutite].

[0015] The ion exchanger of permutite can be prepared easily. For example, it is obtained by making the fusibility salt water solution of the metal which should be carried out the ion exchange to A mold zeolite fully contact. As a metal salt, a chloride, a nitrate, a sulfate, or an organic-acid salt is mentioned. 1–10 micrometers of metal replacement permutite as an adsorbent for heat pump of this invention are 2–8 micrometers still more preferably preferably the mean particle diameter of 0.1–20 micrometers.

[0016] If the particle size of metal replacement permutite is too detailed, a zeolite disperses and is not desirable [this] in case this makes the inside of a heat pump system a vacuum with a vacuum pump. Moreover, in the zeolite of the diameter of a large drop, composition of a original object is difficult. The range of particle size is decided for the above reason.

[0017] Moreover, you may corn the metal replacement permutite as an adsorbent for heat pump of this invention to granularity. The magnitude of the granulation at this time is preferably corned to 10–30 micrometers 10–100 micrometers on an average. The approach of a granulation is good by the approach usually performed industrially.

[0018] Next, zeolite-drainage system heat pump is explained. By making high the substitutional rate which permutes Na ion of the permutite to be used with other metal ions, this zeolite-drainage system heat pump can design very efficient heat pump.

[0019] Here, if a substitutional rate is made high, it will explain why it is desirable when using it as heat pump. A mold zeolite has the presentation of $NaAlSi_3O_8$ and nH_2O at the time of composition. Na ion and an H_2O molecule are got blocked in the opening in the silicate framework in this zeolite crystal structure. This water molecule wears and heat exchange is performed by — **. This heat exchange is the principle of this heat pump system. In that case, in A mold zeolite, the heat exchange (henceforth referred to as hydration enthalpy and ΔH) of 60–67kJ extent is possible per one mol of water molecules, and it seldom depends for this value on the class of convertibility cation. That is, the total amount of heat exchange has a large place depending on the number of the water molecules in an opening.

[0020] Then, if the Q value (heat exchange ability) for evaluating heat exchange is expressed, the heat exchange ability Q will become the following formula.

$Q = \Delta H \times \Delta m_h$ [inside of formula, Q: heat exchange ability (kJ/kg (zeolite)), and ΔH : hydration enthalpy (kJ/mol(water)), and the amount of Δm_h : hydration (a mol(water)/kg (zeolite))]

[0021] That is, the heat exchange capacity Q per zeolite 1000g is $Q = \Delta H - (W/100) - (1000/18) = 0.55$ and $\Delta H - W$, when the effective moisture content in a zeolite is made into W %. (kJ/kg)

It is given.

[0022] From the above-mentioned reason, the absolute value of hydration enthalpy can call greatly what has the high

capacity as a zeolite for heat pump what has the high content of water. Since the value of hydration enthalpy does not change a lot depending on a presentation at this time, it mainly depends for the capacity of the zeolite for heat pump on moisture content. Therefore, rising is important. Since a zeolite can permute a convertibility cation easily, if a divalent cation permutes univalent cations (Na etc.), the number of cations can become half, and it can make the room of water to enter able to increase, and can rise.

[0023] Although it must be still better if a trivalent cation etc. introduces the cation of many ** more, it is difficult to introduce the cation more than trivalent generally. Therefore, in here, they are metal ions, such as a divalent cation, for example, Mg^{2+} , calcium $^{2+}$, Ba^{2+} , Sr^{2+} , Mn^{2+} , Co^{2+} , nickel $^{2+}$, Cu^{2+} , Cd^{2+} , Zn^{2+} , germanium $^{2+}$, Sn^{2+} , or Pb^{2+} . In this, K^{+} , Mg^{2+} , and Co^{2+} are suitable.

[0024] Thus, the content of the moisture in a zeolite can be made [many] more by making the substitutional rate of a cation (metal ion) high. Thus, if a zeolite with many moisture contents to constitute is used as an adsorbent for heat pump, the exchangeable heating value per kg increases, for example, and heat pump with the sufficient effectiveness which is not in the former can be created.

[0025] Next, with reference to a drawing, the heat pump (equipment) concerning this invention is explained. Drawing 1 is the configuration explanatory view of the heat pump which used the adsorbent of this invention. Heat pump 10 is arranging two or more zeolite beds 13 in the tank 11 which installed the heater 15 for heating. And the heat pump system is formed with the pipe 21 which connects the zeolite bed 13 and the water receptacle 20, and the pipe 23 connected to a vacuum pump 30. In addition, the vacuum gage 33 is arranged in pipe 23 way. Moreover, signs 1-6 are the cocks for pipe closing motion. Heat pump 10 fills up a glass tube with metal replacement permutite powder, and forms zeolite ** DDO 13. Two or more zeolite ** DDO 13 is put into the tank 11 which installed the heater 15, and it connects with a sump. First, evacuation of the inside of a heat pump system is carried out with a vacuum pump 30.

[0026] Next, at a heater 15, being [no tank 11] water is warmed and the zeolite bed 13 is heated in a molten bath. The metal replacement permutite powder in the zeolite bed 13 is dehydrated with heating. At this time, the steam dehydrated from the zeolite is cooled at a pipe 21 passage way room temperature, is condensed in the water receptacle 20, and is stored as water. The cock 2 who connects with the water receptacle 20 is closed after dehydration, it exchanges in the water of a room temperature except for the molten bath of a tank 11, and a zeolite is cooled to a room temperature. If a cock 2 is opened, the zeolite which is a super-vacua will evaporate the water of a puddle, and it is begun to absorb it after cooling. At this time, evaporation heat is taken by rapid evaporation and the upper part of the water of a puddle begins to freeze after several minutes. It gets cold slowly and will be in a supercooling condition from it. And when it cooled to -12 degrees C, the whole sump froze in an instant.

[0027] Although the case where the gestalt of this operation carries out evacuation of the inside of a heat pump system is shown, ordinary pressure is sufficient as the inside of a heat pump system. For example, a vacuum is desirable when dehydrating a zeolite at 100 -degree C low temperature. Moreover, when dehydrating a zeolite at a 160 -degree C elevated temperature, it is not necessary to necessarily make the inside of a heat pump system into a vacuum, and ordinary pressure is sufficient. When this is related to the amount of dehydration of a zeolite and it dehydrates at low temperature (100 degrees C or less) If the inside of a heat pump system is not made into a vacuum, when dehydrating at an elevated temperature (160 degrees C) to the ability not to dehydrate sufficient moisture content (about 15 to 17 wt%) It is because sufficient moisture content (about 15 to 17 wt%) can be dehydrated even if the inside of a heat pump system is not necessarily a vacuum.

[0028] The heat pump which used this for the adsorbent list for heat pump of this invention explained above can be used for various fields. For example, it is the air conditioning of cooling of IC base of a computer etc., warm temperature use of a cold district, a dried flower, low-temperature desiccation, and a residence etc.

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EXAMPLE

(Example) Hereafter, an example is shown and this invention is explained still more concretely. When the measuring method of the rate of the cation exchange in this example (rate of charge exchange) carries out quantitative analysis of alkali, alkaline earth metal, and aluminum and Si with an atomic absorption method and the mole ratio of exchanged metal Mn^{+} and Na^{+} is set to $mMmNa$, respectively, the rate of the cation exchange is $nxmM/(nxmM+mNa) \times 100$ (%). It becomes. Moreover, moisture content was calculated as a rate of dehydration in 800 degrees C by thermogravimetric analysis (TG) as a measuring method of moisture content.

[0030] Example 1 (1) The chemical analysis of permutite, the rate of the cation exchange (rate of charge exchange), and moisture content (wt%) are shown in Table 1.

[Table 1]

サンプル	化学式	陽イオン交換率(%)	含水量(wt%)
Na-A	$Na_{1.15}(Al_{1.14} \cdot Si_{1.11})O_4 \cdot 4.21H_2O$	0	21.65
K-A	$(K_{1.13} \cdot Na_{0.21})(Al_{1.13} \cdot Si_{1.01})O_4 \cdot 3.84H_2O$	84.79	18.13
Ca-A	$(Ca_{0.14} \cdot Na_{0.21})(Al_{1.03} \cdot Si_{1.15})O_4 \cdot 4.62H_2O$	89.04	23.46
Mg-A	$(Mg_{0.18} \cdot Na_{1.01})(Al_{1.11} \cdot Si_{1.01})O_4 \cdot 5.34H_2O$	48.94	26.30
Co-A	$(Co_{0.11} \cdot Na_{0.19})(Al_{1.11} \cdot Si_{1.01})O_4 \cdot 5.90H_2O$	64.81	27.13

[0031] According to this result, it turns out that the permutite (sample Mg-A, Co-A) which permuted Mg and Co has high moisture content. This and the permutite which permuted Mg and Co show that it has high heat exchange ability, when using it as an adsorbent for heat pump including a lot of moisture.

[0032] (2) Subsequently, the rate of dehydration (wt%) when heating the sample of Table 1 in atmospheric air (under ordinary pressure) is shown in Table 2. After maintaining the heating approach for 1 hour, it was cooled radiationally in the desiccator and measured sample weight in the place which carried out weighing capacity of the sample of the above-mentioned table 1 into the porcelain crucible, carried out the temperature up with the electric furnace, and became request temperature.

[Table 2]

サンプル	25~100 ℃	25~200 ℃	25~300 ℃	25~400 ℃	25~500 ℃	25~600 ℃	25~700 ℃	25~800 ℃
Na-A	4.23 (wt%)	16.65	19.11	20.66	21.49	21.65	21.66	21.65
K-A	3.21	11.46	16.85	17.87	18.05	18.09	18.12	18.13
Ca-A	4.12	13.90	21.07	21.94	22.45	22.93	23.17	23.46
Mg-A	6.48	20.47	23.52	24.71	25.26	25.68	25.98	26.30
Co-A	8.56	20.44	24.14	25.91	26.50	26.76	26.99	27.13

[0033] From this result, the permutite (sample Mg-A, Co-A) which permuted Mg and Co is understood that the rate of dehydration from low temperature (25~200 degrees C) is comparatively high. This shows that it has high heat exchange ability with heating at low temperature, when using it as an adsorbent for heat pump.

[0034] (3) The relation of the Q value (heat exchange ability) for every dehydration temperature is shown in Table 3.

[Table 3]

脱水温度 θ d/°C	40	60	80	100	120	140	160	180
	$Q_s/\text{kJ} \cdot \text{kg}^{-1}$							
Na-A	137	179	279	505	621	669	665	662
K-A	92	155	226	302	509	599	674	678
Ca-A	133	212	288	371	486	614	718	789
Mg-A	161	394	517	690	759	805	838	865
Co-A	219	350	521	630	685	748	826	864

[0035] Moreover, the above-mentioned relation is shown in the graph of drawing 2. In addition, since sample K-A has good thermal stability, the data to 350 degrees C are shown.

[0036] Example 2 (property measurement of the water content by the substitutional rate of Mg permutation permutite) Mg ion permuted the Na-A type composition zeolite. The result is shown in Table 4. Dehydration temperature was 100 degrees C, and vacuum suction of it was carried out with the rotary pump for 1 hour, and it was performed.

[Table 4]

試料	置換率	試料重量	脱水量	水和量	水和の 割合	水和熱 量	完全水 和熱量	水和開 始温度	温度変 化	含水率
(単位)	%	W(g)	Wd(%)	Wh(%)	Δ H(kJ/mol)	Q(kJ/kg)	Q'(kJ/kg)	(°C)	(°C)	(wt%)
M-1	37.73	0.24826	18.34	16.27	65.61	592.83	668.44	17.13	0.085126	24.69
M-2	41.38	0.25423	18.01	16.95	64.64	608.84	650.09	17.94	0.089568	25.54
M-3	41.84	0.25155	17.75	16.72	64.09	595.36	632.02	16.26	0.088495	25.45
M-4	44.24	0.24760	17.99	16.81	64.51	602.60	644.85	15.69	0.087379	25.61
M-5	47.58	0.26114	17.07	14.90	67.41	557.98	639.15	16.62	0.085529	25.88
M-6	52.56	0.26059	16.01	13.62	65.35	494.48	581.29	17.61	0.075674	26.74
M-7	64.74	0.26495	16.81	15.55	64.61	558.18	603.29	17.46	0.086733	26.48
M-8	65.21	0.26427	17.14	15.34	65.85	561.05	626.94	16.97	0.086069	26.51
M-9	67.85	0.26096	17.57	15.42	65.73	563.20	641.69	17.38	0.089161	26.88

[0037] according to this, 37.73% permutite of Mg permutations is received — the difference of the water content (moisture content) of 67.85% permutite of Mg permutations is 2.19wt%. Furthermore, it turns out that it will become 8.1wt(s)% of increment if it is made a ratio with the whole quantity of water, and it has high heat exchange ability, so that there are many permutations of Mg.

[0038] Mg permutation A mold zeolite (sample name: Mg-A) (Nippon Chemical Industrial Co., Ltd. make, trade name "ZEOSUTA GA-100P") 350g of example 3 example 1 was put into the glass tube (13) of six 3cm outer diameters, and it connected with the tank (11) containing water. .. Refer to drawing 1 [0039]. Subsequently, evacuation of the inside of a heat pump system was carried out, and the vacua was checked with the gage 33. Subsequently, it heated to about 100 degrees C at the heater 15 of a tank 11. At this time, the steam which the zeolite in a glass tube was dehydrated and was dehydrated from the zeolite is cooled at a pipe 21 passage way room temperature, is condensed in the water receptacle 20, and is stored as water. A cock 2 is closed after dehydration and it exchanges in the water of a room temperature except for the molten bath of a tank 11. The dehydrated Mg permutation A mold zeolite is cooled to a room temperature.

[0040] If a cock 2 is opened, the zeolite which is a vacua will evaporate the water of a puddle and it is begun to absorb it after cooling. At this time, evaporation heat is taken by rapid evaporation and the upper part of the water of a puddle begins to freeze after several minutes. It got cold slowly, changed into the supercooling condition, it became -12 degrees C, and the whole sump froze in an instant.

[0041] As a result of using the metal replacement permutite of the following table 5 instead of the Mg permutation A mold zeolite (sample name: Mg-A) of four to example 6 example 3 and also carrying out like an example 3, water was able to be frozen like the example 3.

[Table 5]

	サンプル
実施例 4	K-A
実施例 5	Ca-A
実施例 6	Co-A

[0042] Sample Na-A shown in Table 1 of an example 1 instead of the Mg permutation A mold zeolite (sample name: Mg-A) of example of comparison 1 example 2 was used, and the same experiment as an example 3 was conducted. Consequently, freezing water took time amount very much, and it turned out that effectiveness is bad.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The configuration explanatory view of heat pump.

[Drawing 2] The graph which shows the relation between dehydration temperature and heat exchange ability.

[Description of Notations]

1, 2, 3, 4, 5, 6 Cock

10 Heat Pump

11 Tank

13 Zeolite Bed

15 Heater

20 Water Receptacle

30 Vacuum Pump

33 Vacuum Gage

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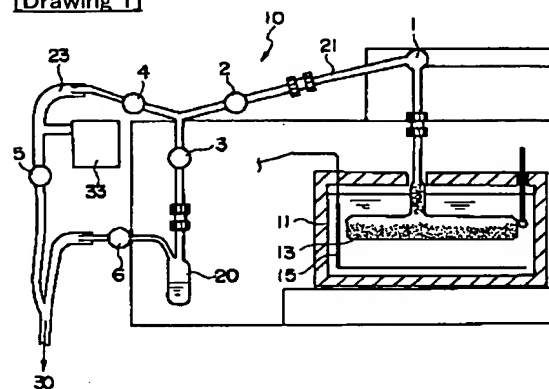
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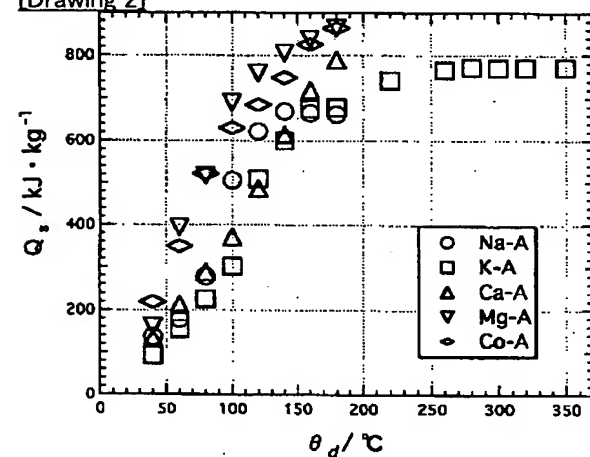
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DRAWINGS

[Drawing 1]



[Drawing 2]



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